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POLYLACTIC ACID COMPOSITION, ITS MANUFACTURING METHOD, AND  
MOLDED ARTICLES OF THE COMPOSITION  
[PORI-NYUSAN SOSEIBUTSU OYOBI SONO SEIZO HOHO NARABI NI  
GAI SOSEIBUTSU NO SEIKEI HIN]

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## Claims:

1. A polylactic acid composition, comprising:  
    polylactic acid comprised of L- and/or D-lactic acid;  
    and  
    polybasic carboxylic acid composition.
2. The polylactic acid composition according to claim 1, further comprising aluminum tris-acetylacetonate.
3. The polylactic acid composition according to claim 1, further comprising 0.00005 to 0.0015 mol% tin octanoate for a lactic acid unit of said polylactic acid comprised of L- and D-lactic acid.
4. The polylactic acid composition according to claim 1, 2, or 3, wherein said polylactic acid is a copolymer of L- and/or D-lactic acid and a segment derived from at least one compound selected from the group consisting of polyalkylene glycol, polyhydric alcohol, hydroxycarboxylic acid, aliphatic polyester, lactone, lactam, and cyclic carbonate.
5. The polylactic acid composition according to claim 1, 2, 3, or 4, wherein said polybasic carboxylic compound is citric acid.
6. A method of manufacturing polylactic acid composition by melt ring-opening polymerization of lactide that is

cyclic dimer of L- and/or D-lactic acid, said method being characterized by performing said polymerization in the coexistence of a polybasic carboxylic acid compound.

7. A method of manufacturing a polylactic acid composition, comprising the step of polymerizing lactide, which is cyclic dimer of lactic acid, and at least one compound selected from the group consisting of polyalkylene glycol, polyhydric alcohol, hydroxycarboxylic acid, aliphatic polyester, lactone, lactam, and cyclic carbonate by melt ring-opening polymerization, said method being characterized by performing said polymerization in coexistence of a polybasic carboxylic acid compound.

8. The method of manufacturing polylactic acid composition according to claim 6 or 7, said method being characterized by using aluminum tris-acetylacetonate as a catalyst for melt ring-opening polymerization of lactide.

9. The method of manufacturing polylactic acid composition according to claim 6 or 7, said method being characterized by using 0.0001-0.003 mol% tin octanoate for said lactide as a catalyst in melt ring-opening polymerization of said lactide.

10. The method of manufacturing polylactic acid composition according to claim 6, 7, 8 or 9, wherein said polybasic carboxylic acid compound is citric acid.

11. A molded article comprised of the polylactic acid composition according to claim 1, 2, 3, 4, or 5.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a polylactic acid composition, its manufacturing method, and a molded article comprised of the composition, which is suitable for powder, fiber, film, and a molding material, which can be used for apparel, household goods, medicinal materials, medical materials, and industrial materials such as the ones for agricultural, fishing industry, industry, and civil engineering and construction.

[0002]

[Conventional Technique]

Since a raw material of polylactic acid is lactic acid obtained by fermenting grains, polylactic acid has attracted attention in place of conventional synthetic polymers made from petroleum in view of earth resource protection. In addition, polylactic acid can be relatively easily hydrolyzed in soil, water, or within a living organism, became lactic acid that widely exists in nature and is not harmful to animals and plants, and lastly decomposed into carbon dioxide and water by metabolism or

biodegradation. Therefore, it has been noted also as biodegradable materials. Especially in these days, since it is highly safe to a living organism, it has been actively applied in medicine and medical fields.

[0003]

For a method of synthesizing polylactic acid, there is a known method, in which lactic acid is oligomerized, lactide, which is cyclic dimer, is isolated by depolymerization, and the lactide is polymerized by ring-opening polymerization. Since high-molecular weight polylactic acid can be relatively easily obtained by this method, this is very useful method as long as lactide is fully purified.

[0004]

Production of polylactic acid by this ring-opening polymerization of lactide can be done by solution polymerization in solvent, but huge equipment is required, manufacturing cost becomes higher, and it is difficult to completely remove a solvent used in the resultant polymer product, so that melt polymerization, which does not require a solvent, is industrially preferred. In case of melt polymerization, the temperature condition of polymerization reaction has to be higher than melting point of the resultant polylactic acid in view of stirring of the

system and taking out after polymerization. For example, in case of poly(L-lactic acid) homopolymer, it has to be at least 180 °C.

[0005]

On the other hand, various types of metal compounds have been already known to having a catalytic effect in the ring-opening polymerization of lactide, and it has been attempted to enhance the polymerization rate by using such compound. Especially, tin octanoate (hereinafter simply referred to as  $\text{Sn}(\text{Oct})_2$ ) has been preferably used in view of that the use has been approved to use as a stabilizer by FDA (Food and Drug Administration).

[0006]

[Problems to be Solved by the Invention]

Polylactic acid is originally colorless transparent polymer, and can be used based on its characteristics. However, since polylactic acid get colored with yellow if left for long time in melted state, polymerization and molding process have to be done quickly in order to obtain colorless polylactic acid. Where the above-described  $\text{Sn}(\text{Oct})_2$  is used as a polymerization catalyst, if it is used more than 0.003 mol% for lactide, the polymerization is completed in a few ten minutes at 180 °C, so that the polylactic acid does not get colored. On the other hand,

if the above-described amount of  $\text{Sn}(\text{Oct})_2$  remains in the polymer, it works as a decomposition catalyst of polylactic acid, so that the molecular weight will dramatically drop, and a molded article with enough strength cannot be obtained. Accordingly, in current situation, a method, in which  $\text{Sn}(\text{Oct})_2$  is removed from polymerization product by reprecipitation or washing, etc. after polymerization, but the manufacturing process becomes complicated and the manufacturing cost also becomes higher.

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[0007]

In addition, if the amount of  $\text{Sn}(\text{Oct})_2$  to use is reduced to not higher than 0.003 mol% for lactide, the resultant polylactic acid will have enhanced heat stability, and the molecular weight reduction upon molding will be less, but the polymerization time has to be at least 100 minutes at 180 °C, and coloration during polymerization is unavoidable.

[0008]

On the other hand, the present inventor first found that polylactic acid obtained by using aluminum tris-acetylacetonate (hereinafter simply referred to as  $\text{Al}(\text{Acac})_3$ ) as a catalyst is extremely superior in heat stability. However, since  $\text{Al}(\text{Acac})_3$  has less catalytic



activity than  $\text{Sn}(\text{Oct})_2$  and requires at least 100 minutes of polymerization time at 180 °C even if a few mol% is used for lactide, coloration is still unavoidable.

[0009]

Therefore, polylactic acid obtained by a method, which is industrially most highly valuable melt ring-opening polymerization of lactide and does not require post treatment after the polymerization has a problems in heat stability and coloration. In view of the above problems, there is provided invention, objects of which is to provide a polylactic acid composition that has less molecular weight reduction and less coloration upon molding, a new method of manufacturing a polylactic acid composition that does not require a post treatment after polymerization in melt ring-opening polymerization, superior in heat stability and has no coloration, and a molded article comprised of the polylactic acid composition.

[0010]

[Means to Solve the Problems]

In order to solve the above objects, the invention comprises polylactic acid comprised of L- and/or D-lactic acid, or copolymer of L- and/or D-lactic acid and a segment from at least one compound selected from the group consisting of polyalkylene glycol, polyhydric alcohol,

hydroxycarboxylic acid, aliphatic polyester, lactone, lactam, and cyclic carbonate, and a polybasic carboxylic acid compound, and further comprises 0.00005 to 0.0015 mol%  $\text{Sn}(\text{Oct})_2$  for lactic acid unit of the polylactic acid.

[0011]

Another aspect of the invention is a method of manufacturing a polylactic acid composition by polymerizing lactide that is cyclic dimer of lactic acid or polymerizing lactide with at least one compound selected from the group consisting of polyalkylene glycol, polyhydric alcohol, hydroxycarboxylic acid, aliphatic polyester, lactone, lactam, and cyclic carbonate by melt ring-opening polymerization, and the method is characterized by performing the polymerization in coexistence of polybasic carboxylic acid compound and using  $\text{Al}(\text{Acac})_3$  or 0.0001 to 0.003 mol%  $\text{Sn}(\text{Oct})_2$  for the lactide.

[0012]

Yet another aspect of this invention is an molded article comprised of polylactic acid, which is polylactic acid comprised of L- and/or D-lactic acid or a polylactic acid composition comprised of L- and/or D-lactic acid and a segment from at least one compound selected from the group consisting of polyalkylene glycol, polyhydric alcohol, hydroxycarboxylic acid, aliphatic polyester, lactone,

lactam, and cyclic carbonate, and a polybasic carboxylic acid compound, and further comprised of  $\text{Al}(\text{Acac})_3$  or 0.0000005 to 0.0015 mol%  $\text{Sn}(\text{Oct})_2$  for a lactic acid unit of the polylactic acid.

[0013]

[Embodiments of the Invention]

Lactide used in this invention is cyclic dimer of lactic acid, which is obtained by oligomerizing lactic acid and then depolymerizing. Lactic acid includes L-lactic acid and D-lactic acid, and accordingly lactide includes L-, D-, meso-, and racemic lactides. Optical purity of lactide used in this invention is not specifically limited, but since the melting point of high-molecular weight polylactic acid is determined by the optical purity of polylactic acid and polylactic acid with higher melting point can be obtained for higher optical purity, it is preferred to use lactide with high optical purity if highly heat resistant polylactic acid is desired.

[0014]

In the ring-opening polymerization of lactide, since a compound having a hydroxyl group works as an initiator, the molecular weight of the resultant polylactic acid is determined by the hydroxyl group concentration in the polymerization raw materials. For example, in case of

homopolymer, in order to obtain polylactic acid having weight-average molecular weight of at least 200,000, the water content in the raw material lactide has to be within range of 5 ppm to 60 ppm. In addition, in case of copolymer, the molecular weight of polylactic acid varies even with hydroxyl group equivalent and amount to mix of the comonomer. If a large amount of comonomer with small hydroxyl equivalent is mixed, i.e. if the hydroxyl group concentration in polymer raw material is larger, the polymerization degree of the resultant polylactic acid is smaller.

[0015]

The polybasic carboxylic acid compound used in this invention is a compound containing at least two carboxyl groups in one molecule. For such compound, oxalic acid, succinic acid, malonic acid, tricarballic acid, citric acid, tartaric acid, terephthalic acid, and so on can be listed, and especially citric acid is preferably used. The amount of such acid to add is not specifically limited, but it is preferably 0.001 wt.% to 1 wt.% for the raw material lactide, and more preferably 0.001 wt.% to 0.1 wt.%.

[0016]

For a catalyst preferably used in a method of manufacturing polylactic acid composition of this

invention, first,  $\text{Al}(\text{Acac})_3$  can be listed. The amount to use  $\text{Al}(\text{Acac})_3$  catalyst in this invention is preferably 0.15 to 5 mol%, and more preferably 0.3 to 3 mol%.

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If it is less than 0.15 mol%, the polymerization degree of polylactic acid is not satisfactory, and if the amount to use is increased, the polymerization degree of the resultant polylactic acid can be increased but the heat stability tends to be reduced. Increase of the polymerization degree becomes saturated around 3 to 5 mol% and if it exceeds this, the polymerization degree is rather reduced.

[0017]

In addition, a next preferably used catalyst in manufacturing a polylactic acid composition of this invention is  $\text{Sn}(\text{Oct})_2$ , but in this case, the amount to use is strictly limited. This is because  $\text{Sn}(\text{Oct})_2$  has high catalyst activity to decomposition of polylactic acid as described above. In order to use the polymer product without purification process such as reprecipitation and washing, the amount to use  $\text{Sn}(\text{Oct})_2$  has to be not higher than 0.003 mol% for lactide. If exceeds this amount, decomposition progresses in the later molding process, and since the polymerization degree reduces, products with

sufficient strength cannot be obtained. In addition, if it is less than 0.0001 mol%, effects of the catalyst can be hardly observed.

[0018]

The polymerization degree in this invention is not specifically limited, but stirring process is necessary for even polymerization, and for this reason, the lower limit of the polymerization temperature is preferably at least melting point of the polymerization product. For example, in case of poly(L-lactic acid) homopolymer, it is preferably at least 180 °C. Furthermore, the upper limit of the polymerization temperature is preferably 200 °C. If the temperature is as high as 200 °C or higher, the polymerization equilibrium between lactide and polymer shifts towards lactide, it becomes harder to increase the polymerization degree, and the production of lactide increases, so that the yield of polymer is reduced.

[0019]

In addition, the time required for polymerization is normally 60 to 6,000 minutes, but since it varies depending on the amount of catalyst used, polymerization temperature, moisture content in the system, type and amount of comonomer in case of copolymer, and so on, time to reach desired polymerization degree can be suitably selected. In

addition, since the polymerization degree of polylactic acid to be produced in this reaction system varies with the moisture content in the system, the reaction system is preferably in an anhydrous atmosphere, and it is preferred to perform the polymerization in inert gas atmosphere, such as nitrogen and argon, or under reduced pressure. In addition, it is also possible to remove remaining lactide by maintaining the polymerization product within temperature range of 110 to 140 °C after the reaction and performing solid-phase polymerization.

[0020]

This invention is applicable for any types of copolymer essentially containing lactic acid, as well as polylactic acid homopolymer. More specifically, by mixing and copolymerizing other monomer, the crystallinity, biodegradation rate, and thermal flowability can be controlled. For monomers having such effects, polyalkylene glycol, polyhydric alcohol, hydroxycarboxylic acid, aliphatic polyester, lactone, lactam, and cyclic carbonate can be listed, and two or more types of the compounds can be also used at the same time.

[0021]

For polyalkylene glycol, for example, homopolymer such as ethylene glycol and propylene glycol and copolymer

thereof, ethylene glycol, propylene glycol, neopentyl glycol, glycerin, trimethylol propane, and so on can be used as the polyhydric alcohol, and glycolic acid, 3-hydroxybutyric acid, 3-hydrovaleric acid, and so on can be used for the hydroxycarboxylic acid. For the aliphatic polyester, homopolymer and copolymer of the above-described hydroxycarboxylic acid or polymer of every sort of aliphatic diol and aliphatic dicarboxylic acid can be used. For lactone,  $\gamma$ -butyl lactone,  $\beta$ -valerolactone,  $\epsilon$ -caprolactone, glycolide, and so on can be used. For lactam,  $\gamma$ -butyrolactam,  $\beta$ -valerolactam,  $\epsilon$ -caprolactam, and so on can be used, and propylene carbonate and so on can be listed for the cyclic carbonate, but they are not limited to those.

[0022]

Molded articles of this invention are articles made by melt-molding the above-described polylactic acid composition of this invention. Examples of such molded articles include any molded articles made by injection or extrusion molding, etc., film or sheet, or unstretched or stretched and orientated fiber, and further include fiber structure made from the fiber (knitted goods, textile, unwoven fabric, paper, string, tape, rope, net, etc.), even further include composite material of the film or sheet and



fiber, such as synthetic leather, but examples are not limited to those.

[0024]

[Working Examples]

Hereunder, the present invention will be fully described with working examples. Before the description, methods of measuring every sort of characteristic values used herein will be described.

[0025]

<Weight-Average Molecular Weight>

Weight-average molecular weight (hereinafter simply referred to as "Mw") of polymer part was measured by GPC (gel permeation chromatography) using chloroform as an eluent. Here, the molecular weight calibration curve was prepared with polystyrene.

[0026]

<Heat Stability Test Method>

For a purpose of heat stability test, a polylactic acid composition was melt-treated by heating under a constant condition. Samples were dried at room temperature under reduced pressure for 24 hours in the presence of phosphorus pentoxide. Then, placing about 3 g of each dried sample in a test tube, each sample was heated for 1 hour in 180 °C oil bath after substituting with nitrogen.

Mw of the polylactic acid composition before melt treatment (before polymerization) and after melt treatment (after melting) was determined by the above-described method, and a sample having heat stability exceeding 70 %, which is determined by the following equation is considered as polylactic acid composition with superior heat stability.

Heat Stability (%) =  $\frac{\text{Mw of polylactice acid (after melting)}}{\text{Mw of polylactic acid composition (after polymerization)}} \times 100$

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[0027]

<Coloration Test>

The polylactic acid composition obtained by the polymerization was pressed while heating to 2 mm thickness with a press machine having hot plate temperature of 180 °C, and thereafter taken out from the machine and rapidly cooled. Placing the resultant sample on white paper, the coloration was evaluated by visual observation.

[0028]

(Working Example 1)

60 g (416 mmol) of L-lactide (with 10 ppm moisture content, manufactured by PURAC Co.), 0.675 g (2.08 mmol) of  $\text{Al}(\text{Acac})_3$ , and 0.06 g of citric acid were placed in a reaction vessel equipped with a stirring device and a

nitrogen inlet tube. After substituting with nitrogen, the mixture was heated to 180 °C in nitrogen gas flow so as to perform ring opening polymerization. At this time, the amount of  $\text{Al}(\text{Acac})_3$ , which is a catalyst, was 0.5 mol for the raw material L-lactide, and the amount of citric acid was 0.1 wt.% similarly. Once molecular weight increase became saturated, the reaction was terminated and the polymerization product was taken out from the system. Characteristics of the resultant polylactic acid composition were as shown in Table 1. The resultant polylactic acid composition was colorless, had Mw of 318,000 after polymerization and had Mw of 277,000 after melt treatment, so that the heat stability was 87.1 % and the composition had extremely superior heat stability.

[0029]

(Comparative Example 1)

Similarly to Working Example 1 except not using citric acid in Working Example 1, polylactic acid composition was obtained. Respective characteristic values were as shown in Fig. 1, and polylactic acid composition that was superior in heat stability, but was colored with light yellow was obtained.

[0030]

(Working Example 2)

Similarly to Working Example 1 except using 0.002 mol%  $\text{Sn}(\text{Oct})_2$  for the lactide as a catalyst in place of  $\text{Al}(\text{Acac})_3$  in Working Example 1, the polymerization was performed. Respective characteristic values of the resultant polylactic acid composition were as shown in Fig. 1, and a polylactic acid composition that was colorless and superior in heat stability was obtained.

[0031]

(Comparative Example 2)

Similarly to Working Example 2 except not using citric acid in Working Example 1, a polylactic acid composition was obtained. Respective characteristic values were as shown in Fig. 1, and polylactic acid composition that was superior in heat stability, but was colored with light yellow was obtained.

[0032]

[Table 1]

		Working Example 1	Comparative Example 1	Working Example 2	Comparative Example 2
Catalyst Catalyst Amount: mol%		Al(Acac) <sub>3</sub> 0.5		Sn(Oct) <sub>2</sub> 0.002	
Amount of Citric Acid Added wt%		0.1	0	0.1	0
Coloration		colorless	light yellow	colorless	light yellow
Mwx10 <sup>4</sup>	After polymerization	31.8	37.8	27.4	26.8
	After melting	27.7	32.5	20.9	21.0
Heat stability (%)		87.1	86.9	76.3	78.4

[0033]

(Working Example 3)

Similarly to Working Example 1 except using 2.4 g of polyethylene glycol PEG 6000 (52 ppm moisture content) as polymerization raw material in addition to L-lactide, the polymerization was performed. Respective characteristic values of the resultant polylactic acid composition were as shown in Table 2, and a polylactic acid composition, which has lower polymerization degree than homopolymer but was colorless and was superior in heat stability, was obtained.

[0034]

(Comparative Example 3)

Similarly to Working Example 4 <3?> except not using citric acid in Working Example 1, polylactic acid composition was obtained. Respective characteristic values were as shown in Fig. 1, and polylactic acid composition that was superior in heat stability, but was colored with light yellow was obtained.

[0035]

[Table 2]

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		Working Example 1	Comparative Example 1
Catalyst Catalyst Amount: mol%		Al(Acac) <sub>3</sub> 0.5	
Amount of Citric Acid Added wt%		0.1	0
Coloration		colorless	light yellow
Mwx10 <sup>4</sup>	After polymerization	11.4	13.1
	After melting	10.1	11.7
Heat stability (%)		88.6	89.3

[0036]

[Effects of the Invention]

Since the polylactic acid composition of this invention is superior in heat stability, molecular weight reduction upon molding process is small and products with high strength can be obtained. In addition, since the composition is colorless, it can be suitably applied in fiber for apparel, every sort of film, and so on. In

addition, since melt ring-opening polymerization is employed for polymerizing lactide in the method of this invention, high molecular weight polylactic acid can be easily obtained, and since it does not require post treatment step such as removal of a solvent, it is highly industrially valuable. Furthermore, since the molded articles of this invention have high strength and are colorless, they are extremely suitable for powder, fiber, film, and a molding material, which can be used in apparel, household goods, medicinal materials, medical materials, and industrial materials such as the ones for agricultural, fishing industry, industry, and civil engineering and construction.